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Hanford Boehmite/Chromium Dissolution Data

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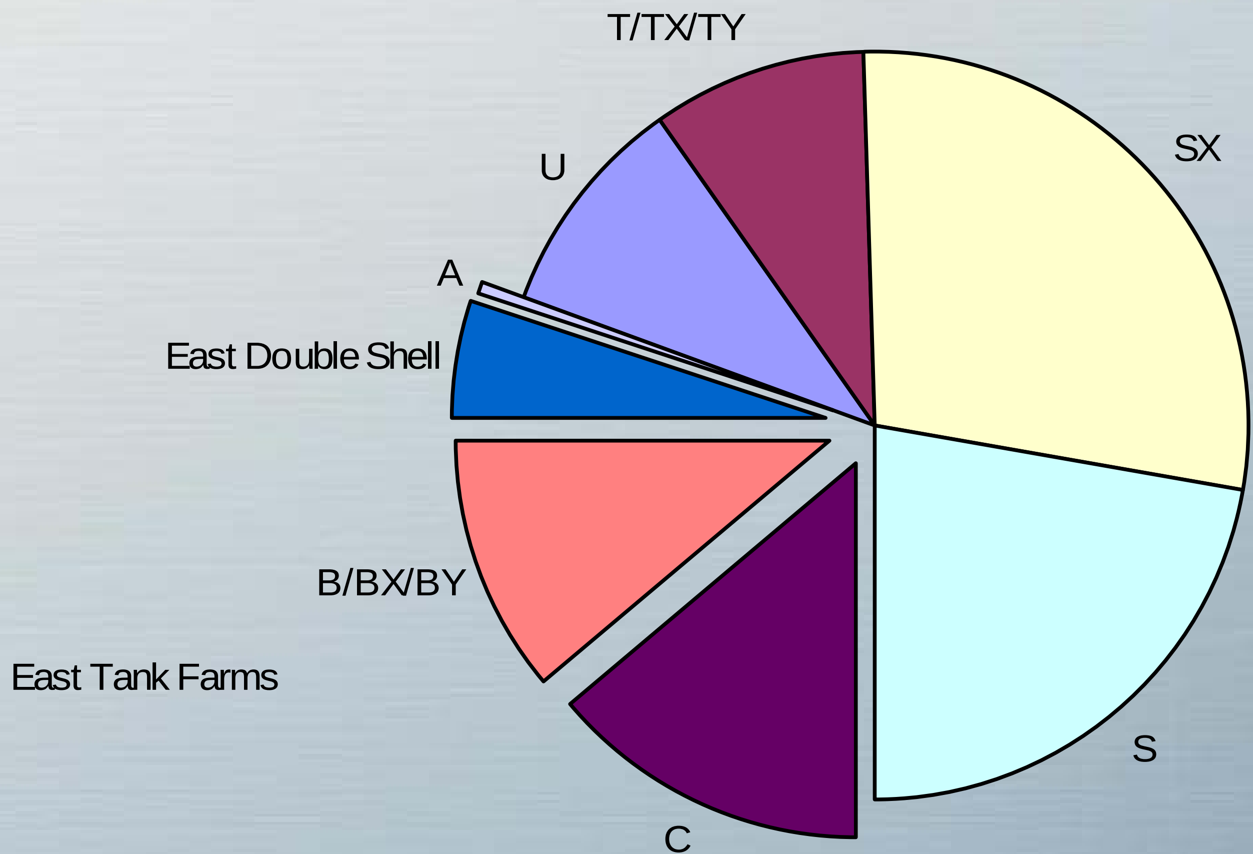
The Problem

- A significant quantity of aluminum and chromium are present in HLW storage in the Hanford tank farm
- Most of this aluminum is insoluble
- Much of the chromium is insoluble as well
- Aluminum doesn’t go into glass well
- Chromium really doesn’t go into glass well
- HLW sludges are to be disposed of in glass

Background

- Most abundant elements in the tanks include Fe, Al, P, Ca, Si, and Bi
- Aluminum is one of the most prevalent elements (nearly 70% of the sludge)
- Aluminum is mainly found in the form of:
  - Gibbsite {$Al(OH)_3$} – as micrometer sized colloidal particles
  - Boehmite {AlOOH} – as agglomerates of nanometer sized particles
- Chromium is a minor component (~ 3%) of the sludge

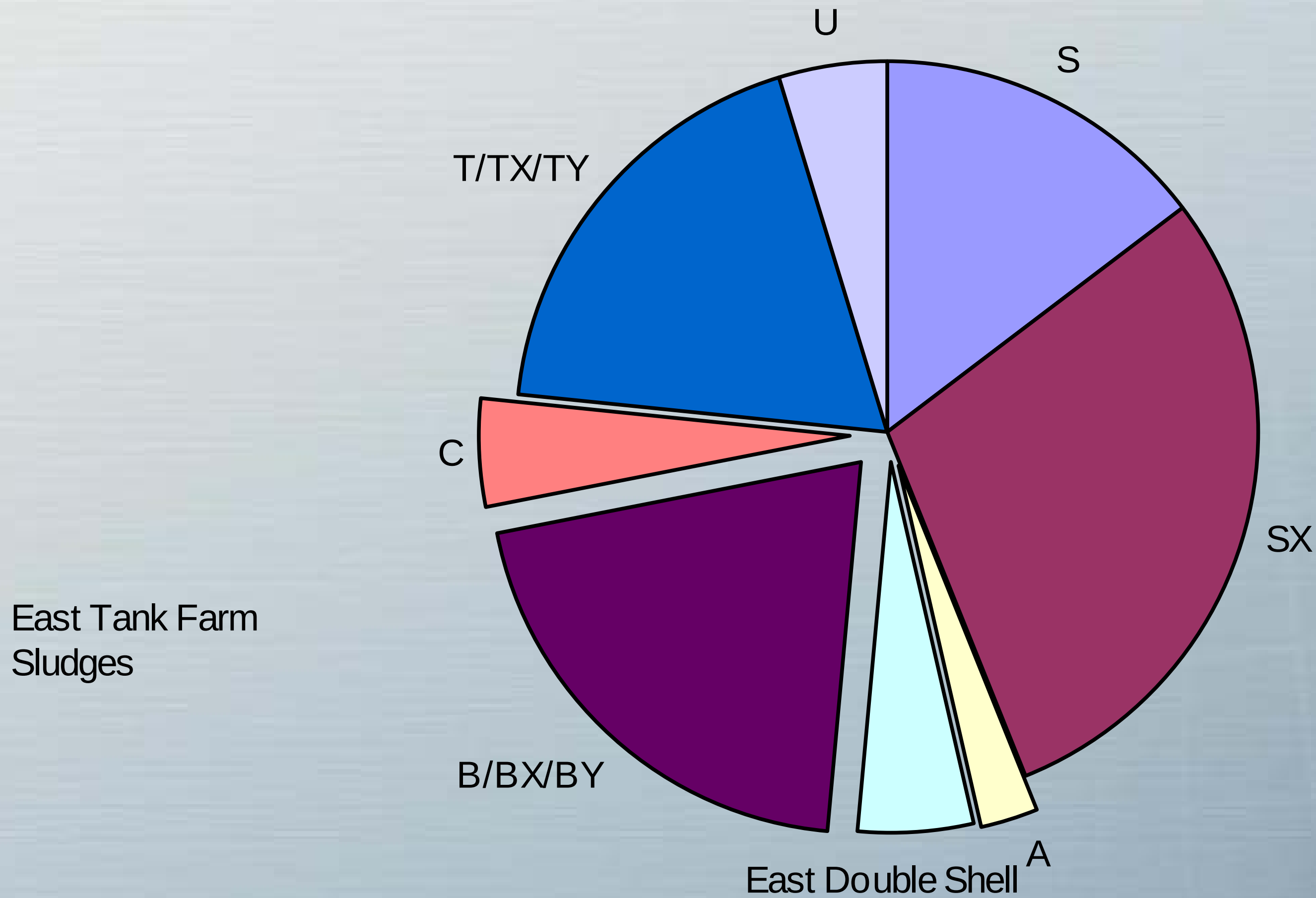
Al Sources in Hanford Sludge Waste



Al key sources

- Redox
  - Contains predominately boehmite
  - Average 90+ % aluminum in solids
  - Average leach factor from BBI of 0.42
- Cladding Waste from Purex
  - Contains predominately gibbsite
  - Average 90+ % aluminum in solids
  - Average leach factor from BBI of 0.8
- Bi-Phosphate saltcake
  - Most samples to date blended with other sludges
- Cladding Waste from Redox
  - Effectively no data
  - Average leach factor from BBI of 0.9

Cr Sources in Hanford Sludge Waste



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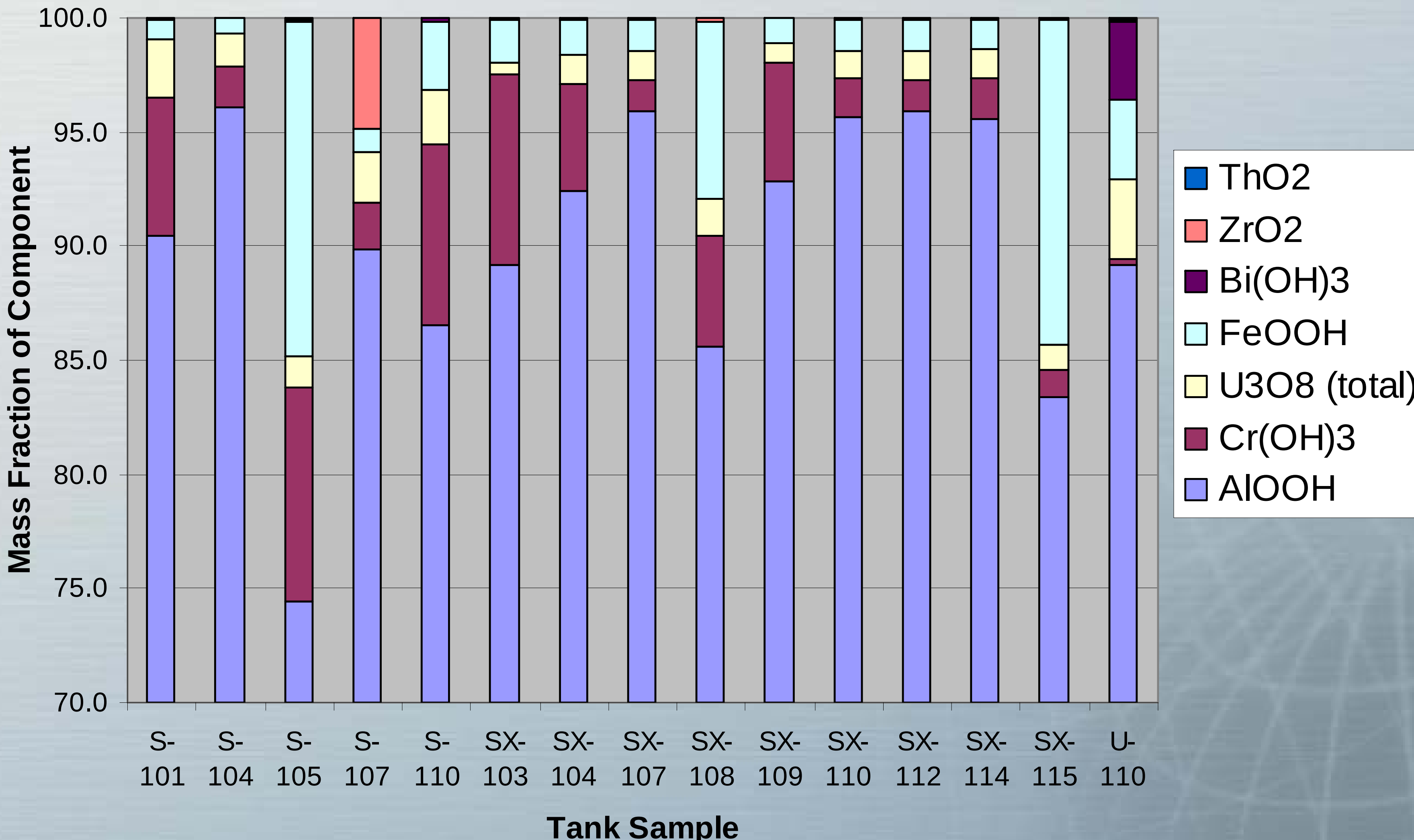
S/SX Sludges

- Predominate Al phase is boehmite
- Gibbsite is easily dissolved by heating with caustic
- Boehmite requires more aggressive conditions (higher temperatures and longer times)
- Dissolution of Cr is simultaneous with aluminum

Composition of Typical S/SX Sludge of Interest



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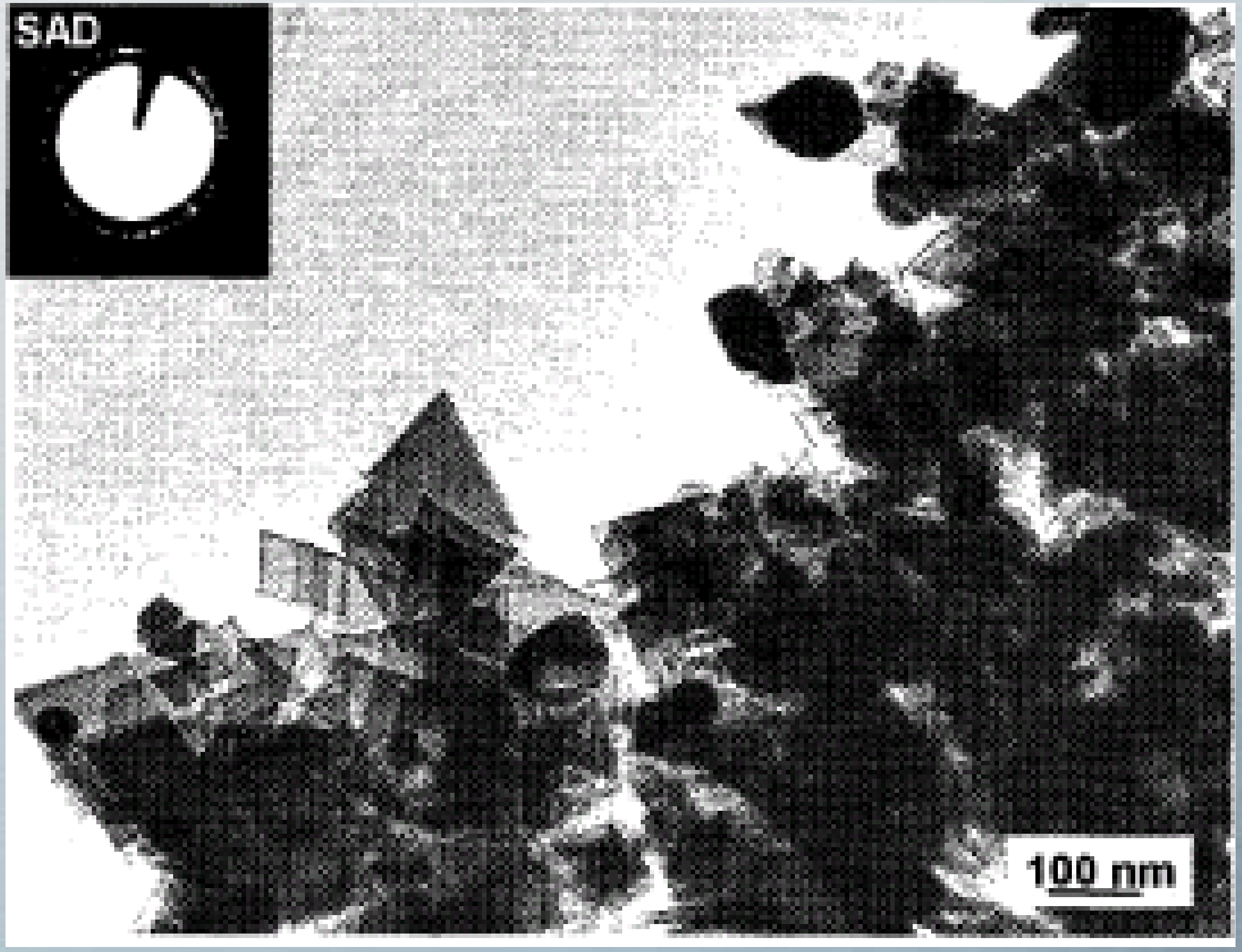
S-104 (Redox) - boehmite



SEM examples from literature

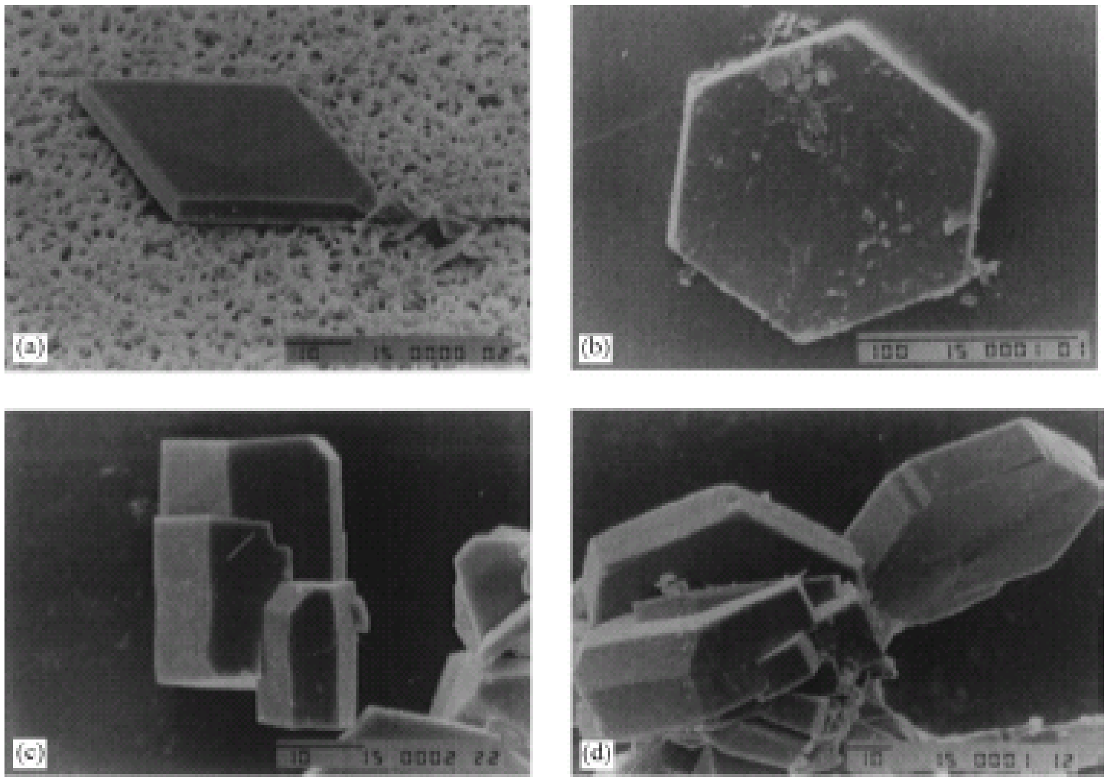
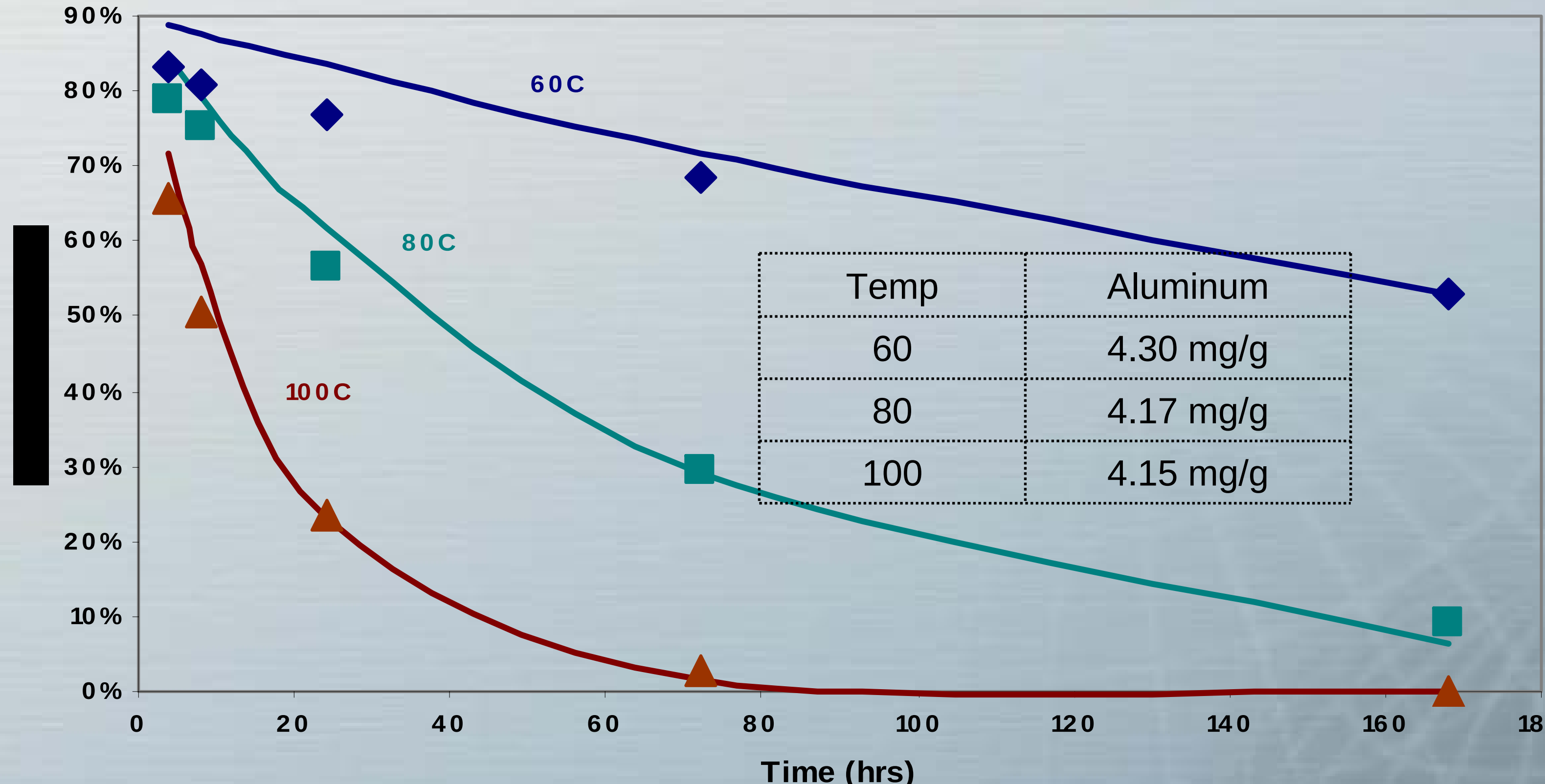


Fig. 1. SEM micrographs showing examples of γ-Al(OH)$_3$ crystal morphologies, with (a) lozenge, (b) hexagon, (c) prisms and (d) agglomerate. The length of the scale bar in the inset is in μm.

Test Protocol

- Typically about 1 g of sludge in 100 mL of caustic in sealed vessel
- Agitated – either stir bar or shaken
- Temperature maintained by a heating block
- Small – 1 mL - samples removed periodically
- Samples analyzed for metal content
- Residual sludge digested and analyzed to complete material balance

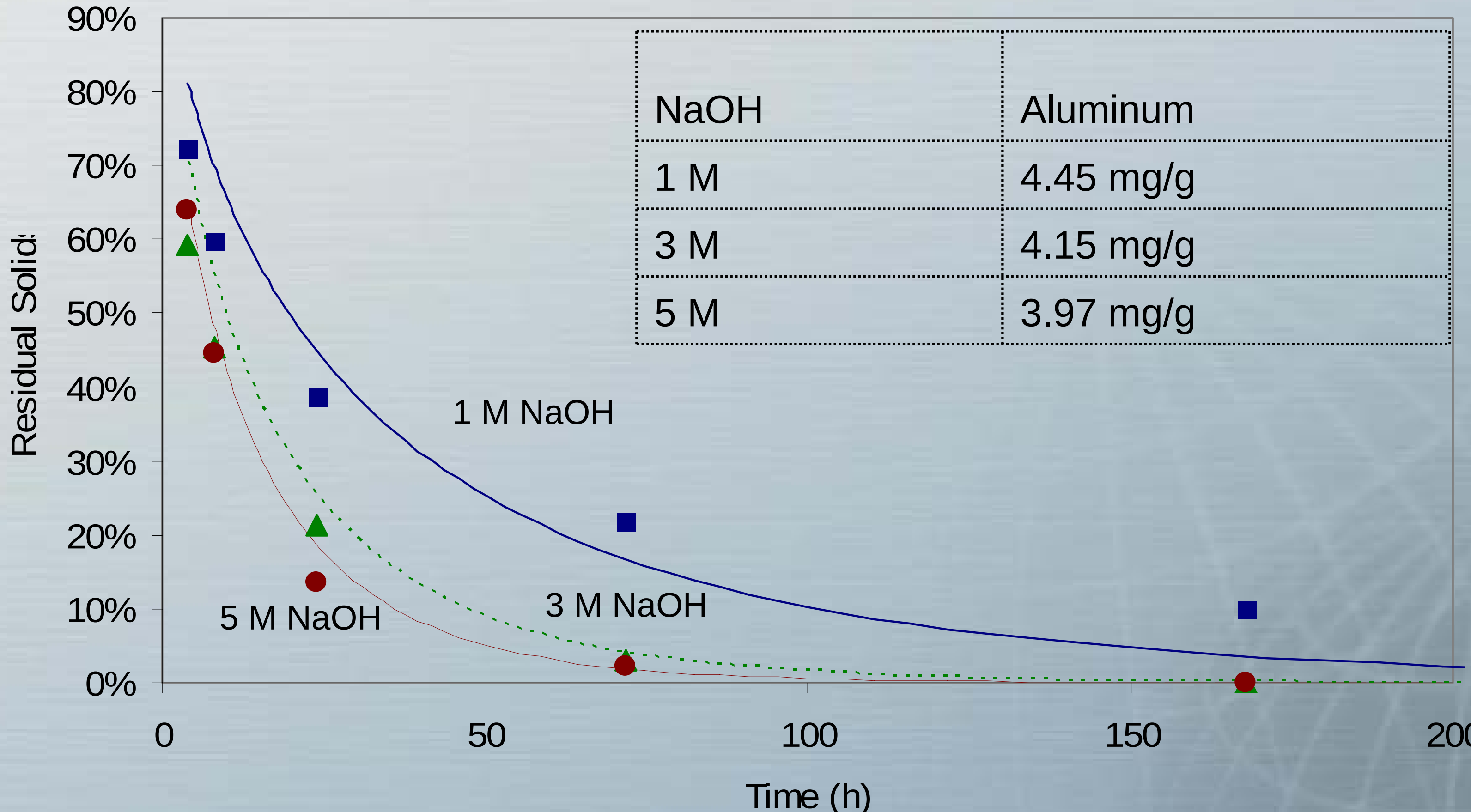
Aluminum Solids (Mass Fraction) for 3 M NaOH in Tank S-110



Temp	Aluminum
60	4.30 mg/g
80	4.17 mg/g
100	4.15 mg/g

Lumetta, G.J. et al., *Caustic Leaching of Hanford Tank S-110 Sludge*. PNNL-13702; Pacific Northwest National Laboratory: Richland, WA, 2001.

S-110 Boehmite Dissolution at 100 ºC



NaOH	Aluminum
1 M	4.45 mg/g
3 M	4.15 mg/g
5 M	3.97 mg/g

Aluminum Sludge Leaching Model

Shrinking particle model modified for a distribution of platelet particles.

Initial Size Distribution of Reactive Aluminum Solids (Gamma distribution)

$$p(L) = \frac{1}{\beta^{\alpha}\Gamma(\alpha)} L^{\alpha-1} e^{-\frac{L}{\beta}}$$

Surface Reaction Rate (Arrhenius Form)

$$k_s = Ae^{-\frac{E}{RT}}$$

Hydroxide Ion Concentration

Reaction time

$$X_B^* = 1 - \int_{L_t}^{L_{\max}} f(L,t)\, p(L)\, dL$$

$$X_B = \frac{C_{Al,e}}{C_{Al,s}} \tanh\left(\frac{k_s C_{OH}^{1/2} C_{Al,s}}{\rho_B L C_{Al,e}} t \right)$$

Aluminum Conversion for distribution of particles

Mass fraction of solid phase Aluminum remaining Using mono-disperse model

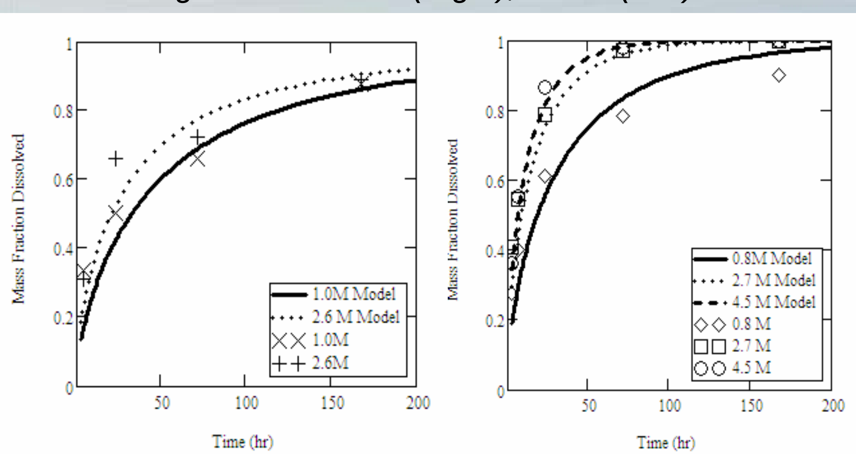
$$f(L,t) = 1 - X_B$$

Ratio of aluminum solubility Limit to total aluminum available for dissolution

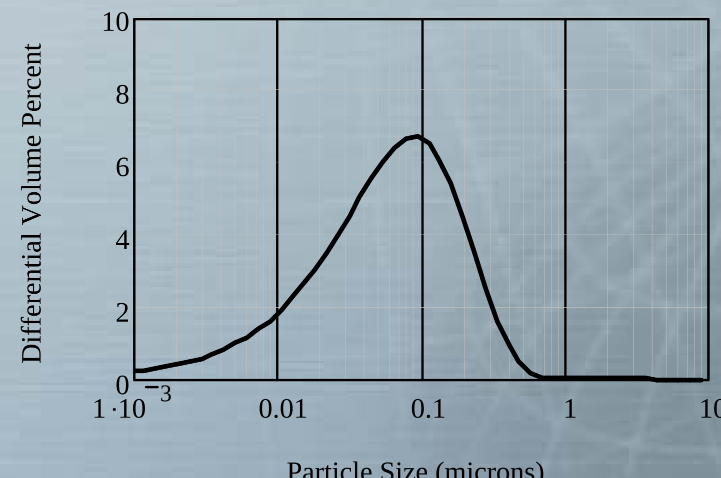
Molar Density of Beohmite

Initial Size of Platelet

Modeling Results S-101 (Right); S-110 (Left)



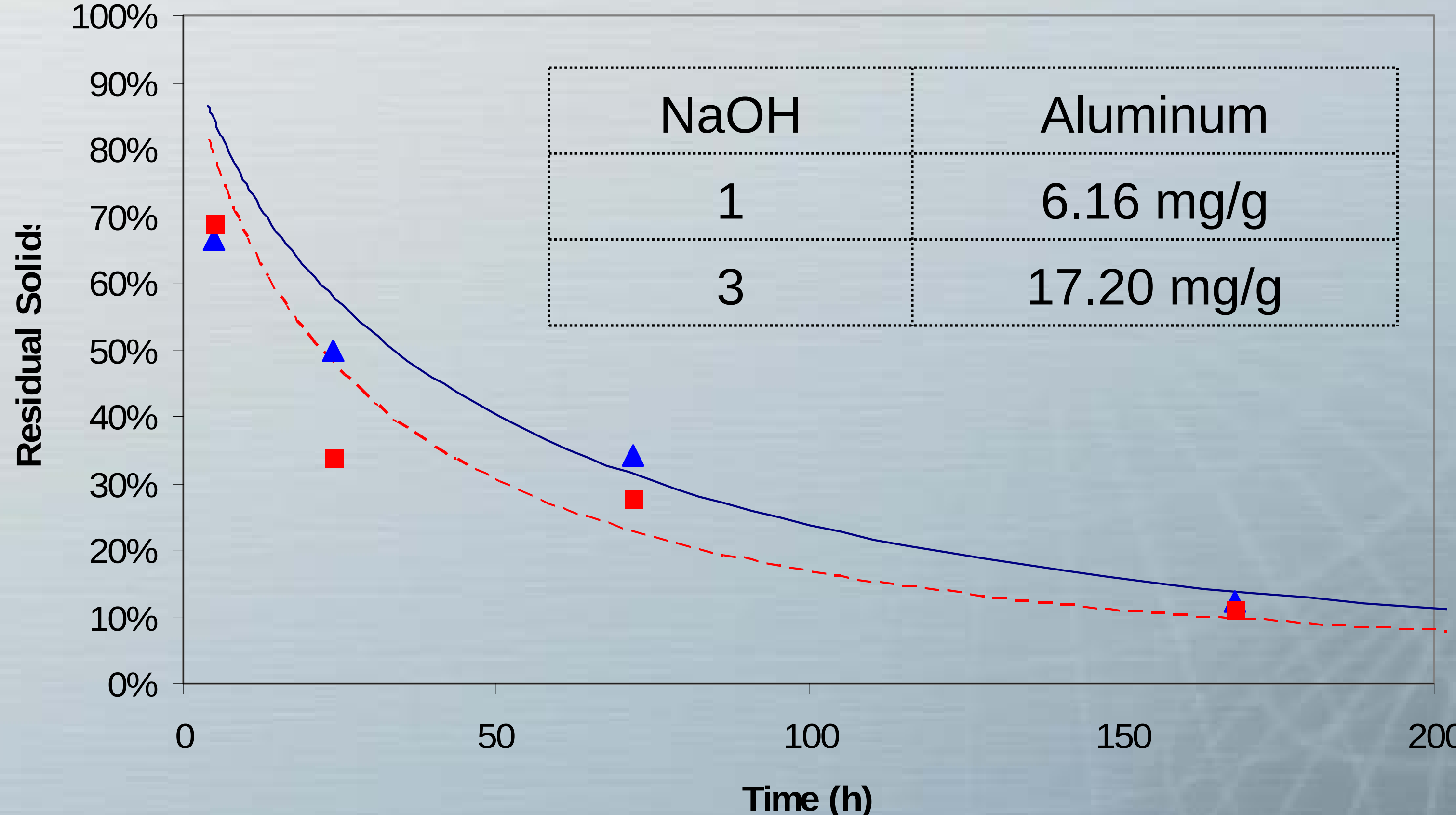
Particle Size Distribution Used in Model



Publication

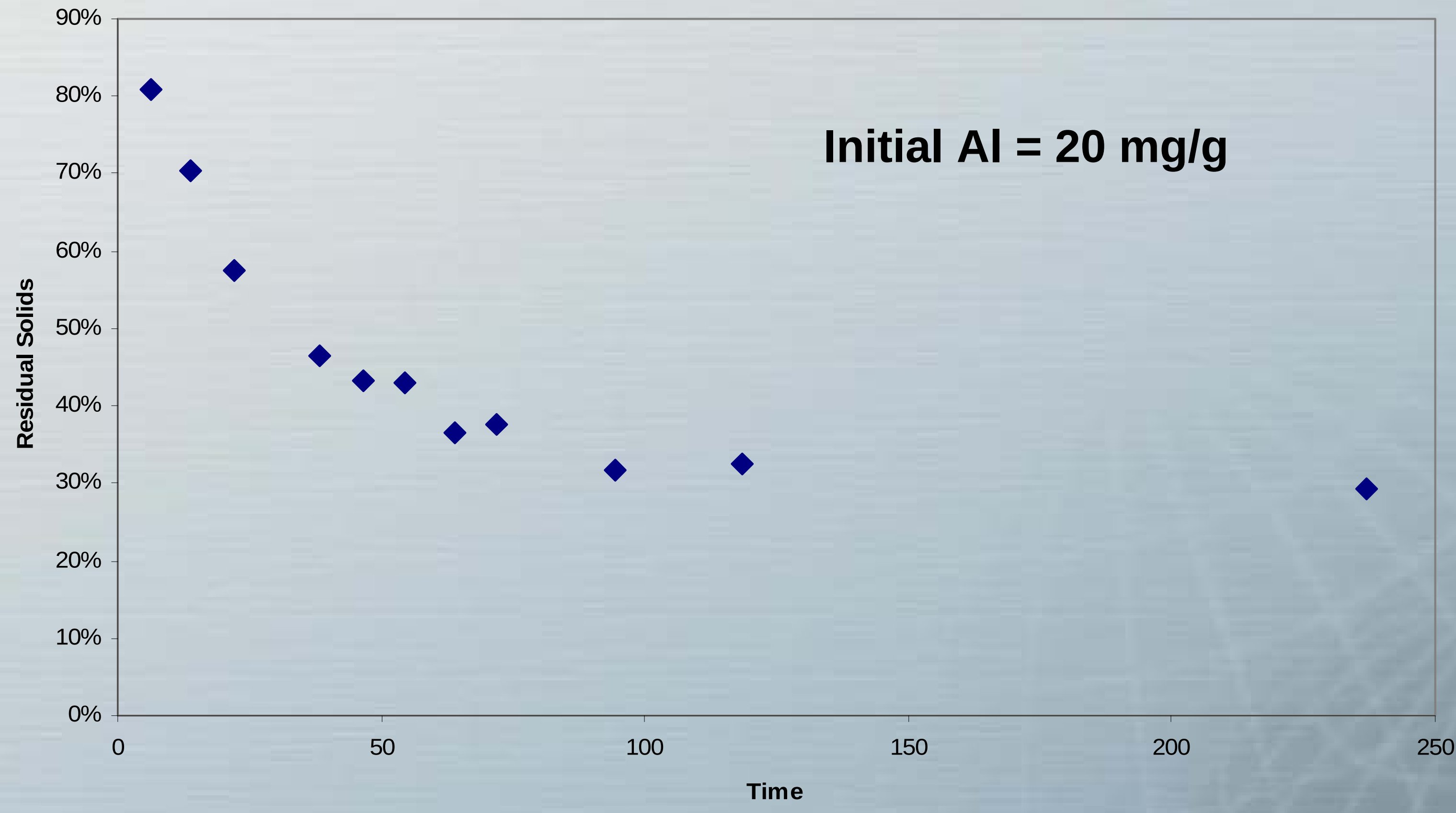
R.A. Peterson, G.J. Lumetta, B.M. Rapko, and A.P. Poloski
“Modeling of Boehmite Leaching from Actual Hanford High-Level Waste Samples” *Sep. Sci. Tec.* (accepted 12/06)

S-101 Boehmite Dissolution at 100 ºC



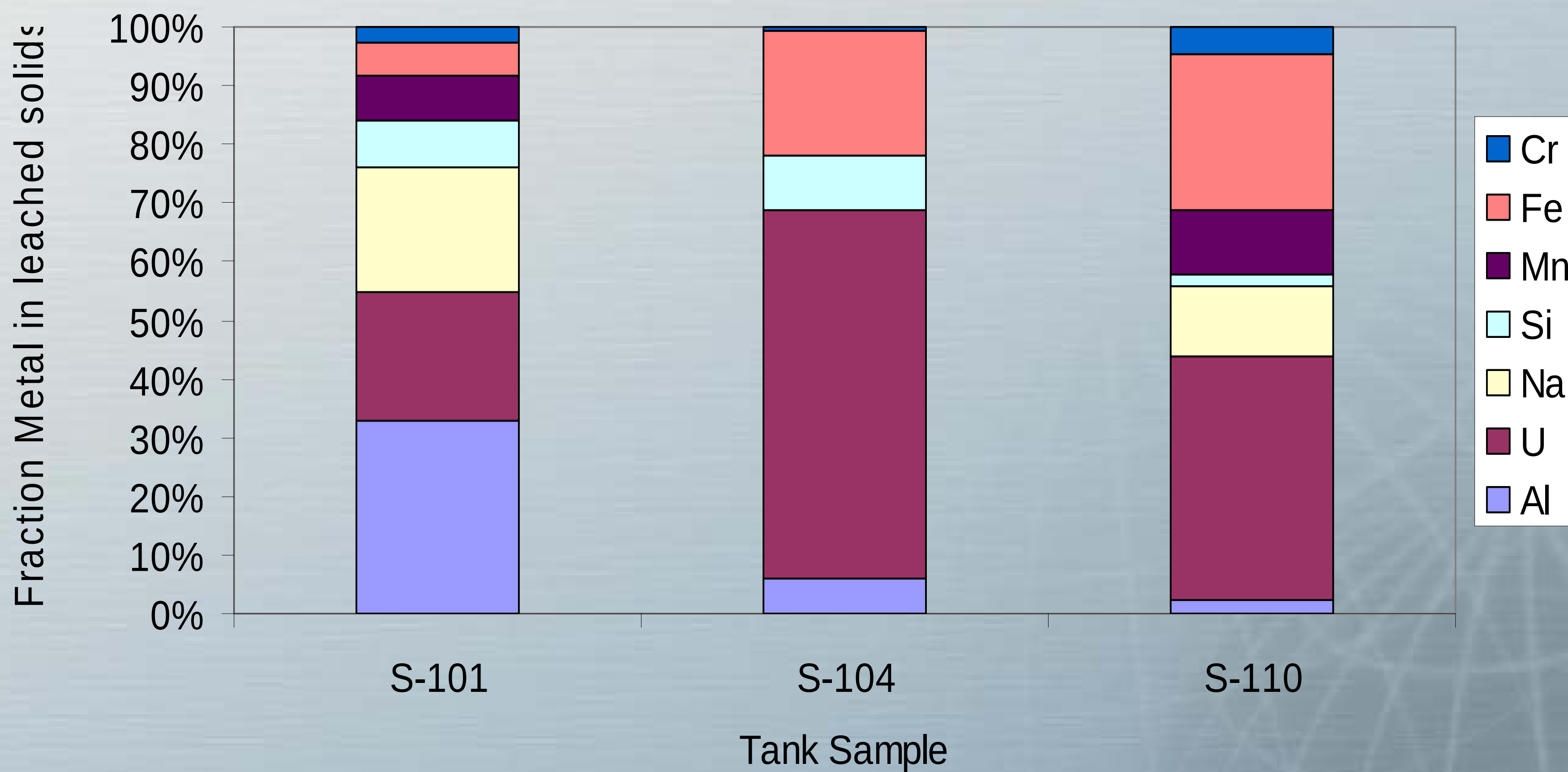
Lumetta et. al. 1998

S-107 Boehmite Dissolution at 100 ºC – 3M NaOH



Brooks et.al, 1998

Composition for Redox waste after extended leach



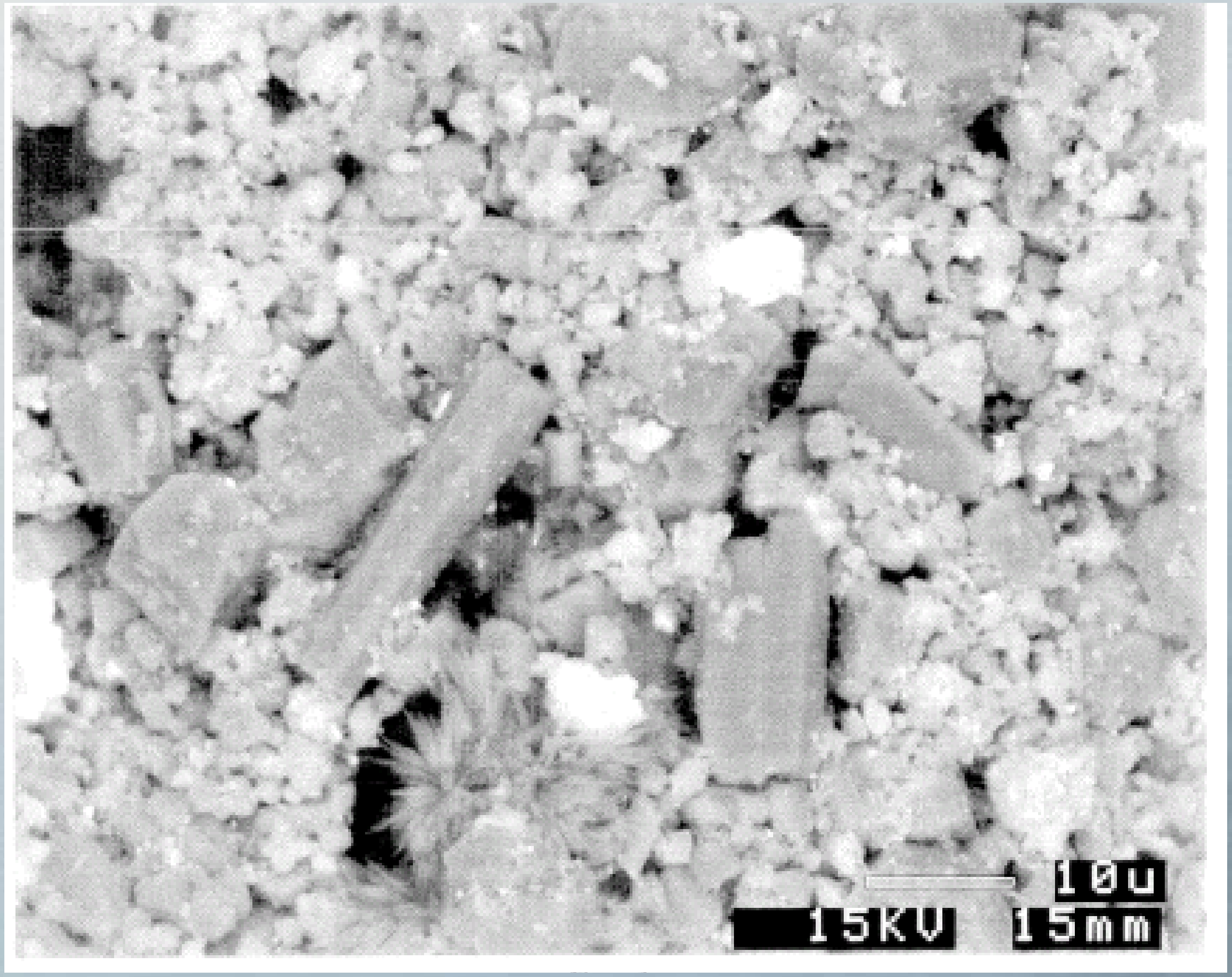
Boehmite Conclusions

- Boehmite can be dissolved from HLW sludge with sufficient time, temperature and caustic
- A model was developed based on the boehmite dissolution rate data
- Additional characterization data (correlated with leaching data) needed to validate dissolution model and to validate simulant development

Gibbsite dissolution data

- Limited testing has been performed with HLW sludge samples containing sludge
- No kinetic information is available for gibbsite dissolution
- Test typically employed 5 or 10 hour contact time at 100 °C with 3 M NaOH.

C-105 example (CWP) - gibbsite



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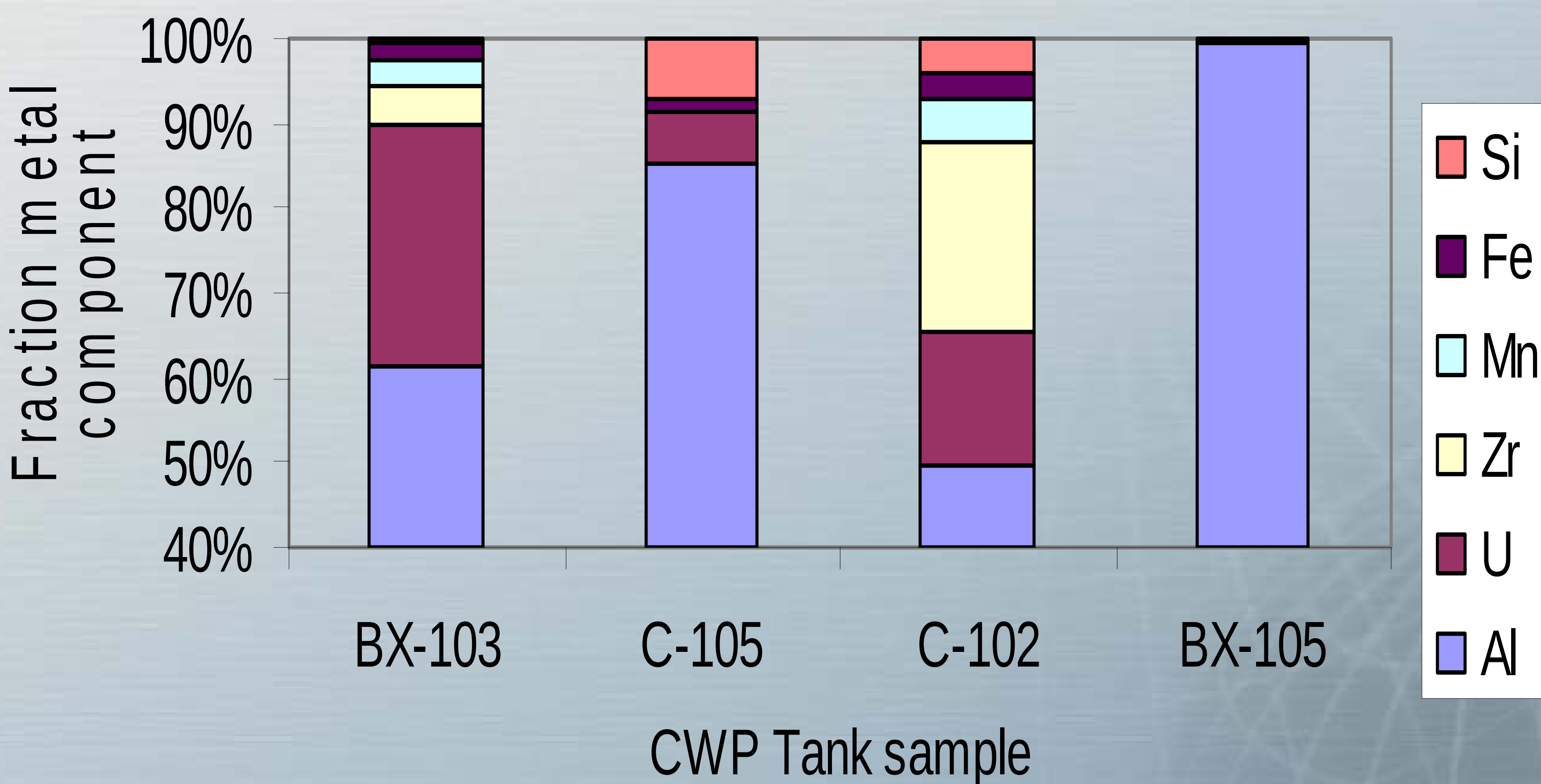
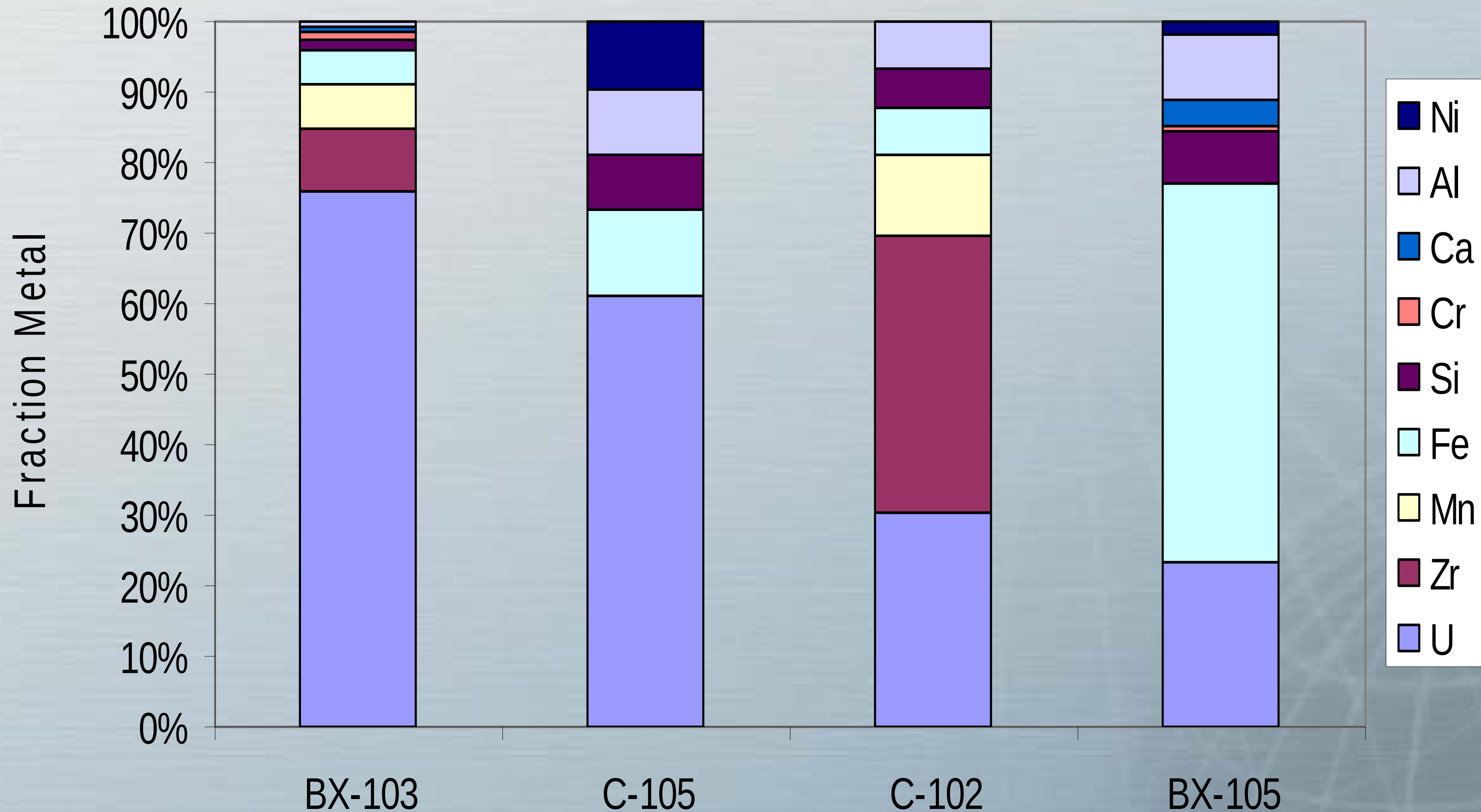
Typical CWP waste before leaching



CWP Composition after leaching



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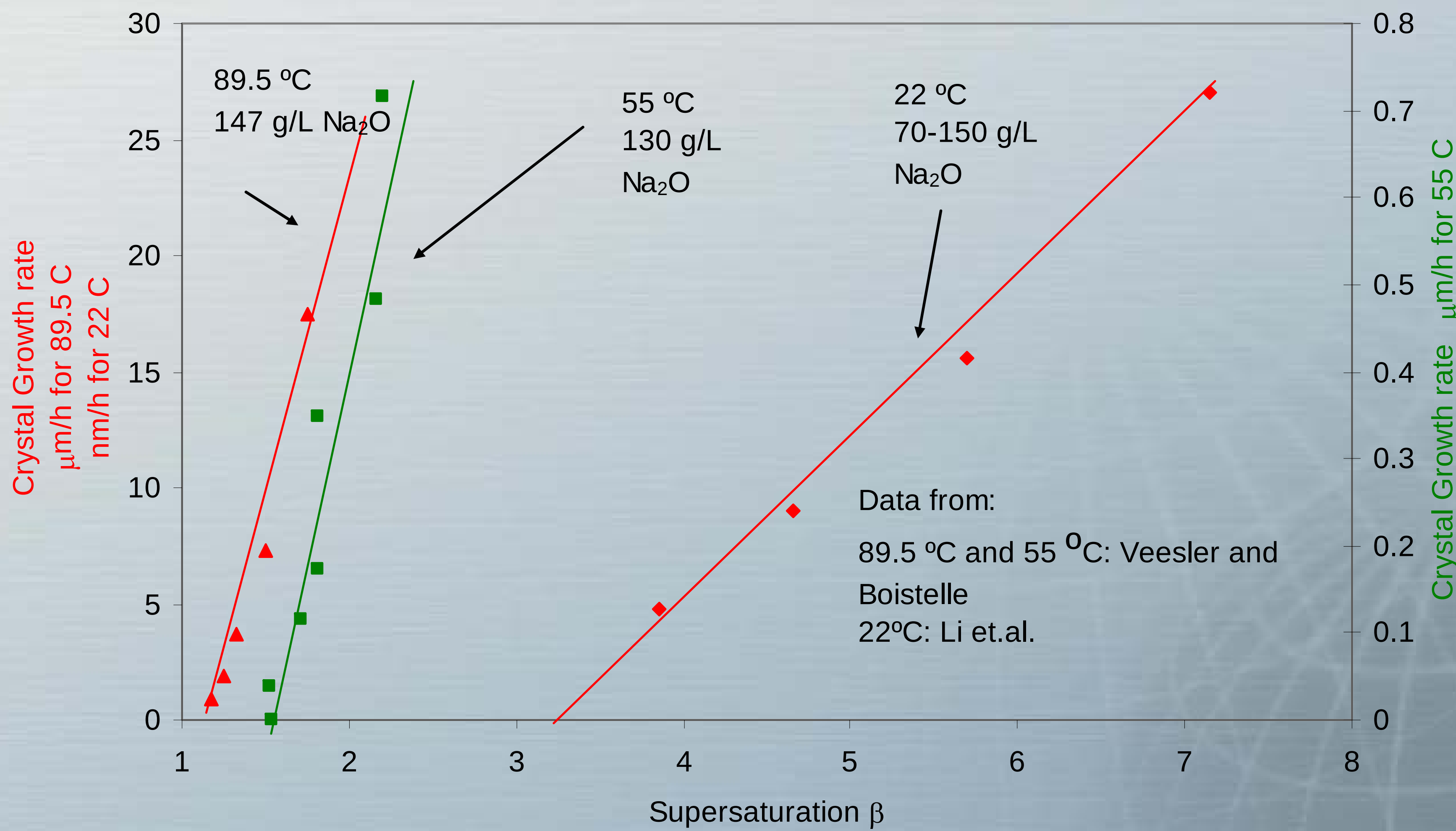
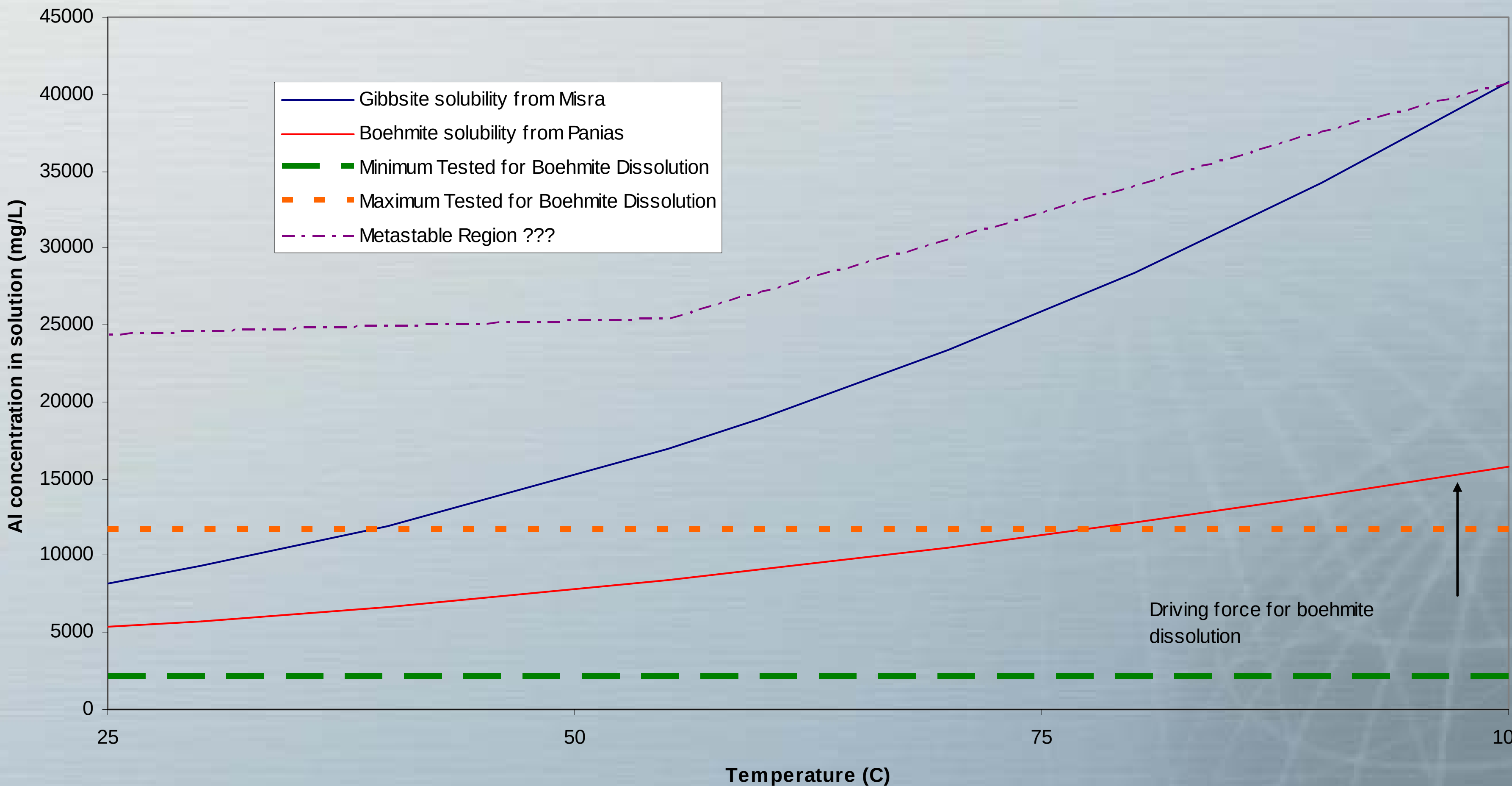
How much caustic is required?

- Avoid precipitation after filtration
  - Dilution can cause precipitation
  - Cooling can cause precipitaton
- Provide sufficient caustic to get adequate kinetics
  - For feeds that are a blend of boehmite and gibbsite, gibbsite will dissolve first and may decrease boehmite dissolution

Recrystallization of gibbsite from supersaturated solutions



Al concentration in 3 M NaOH solution



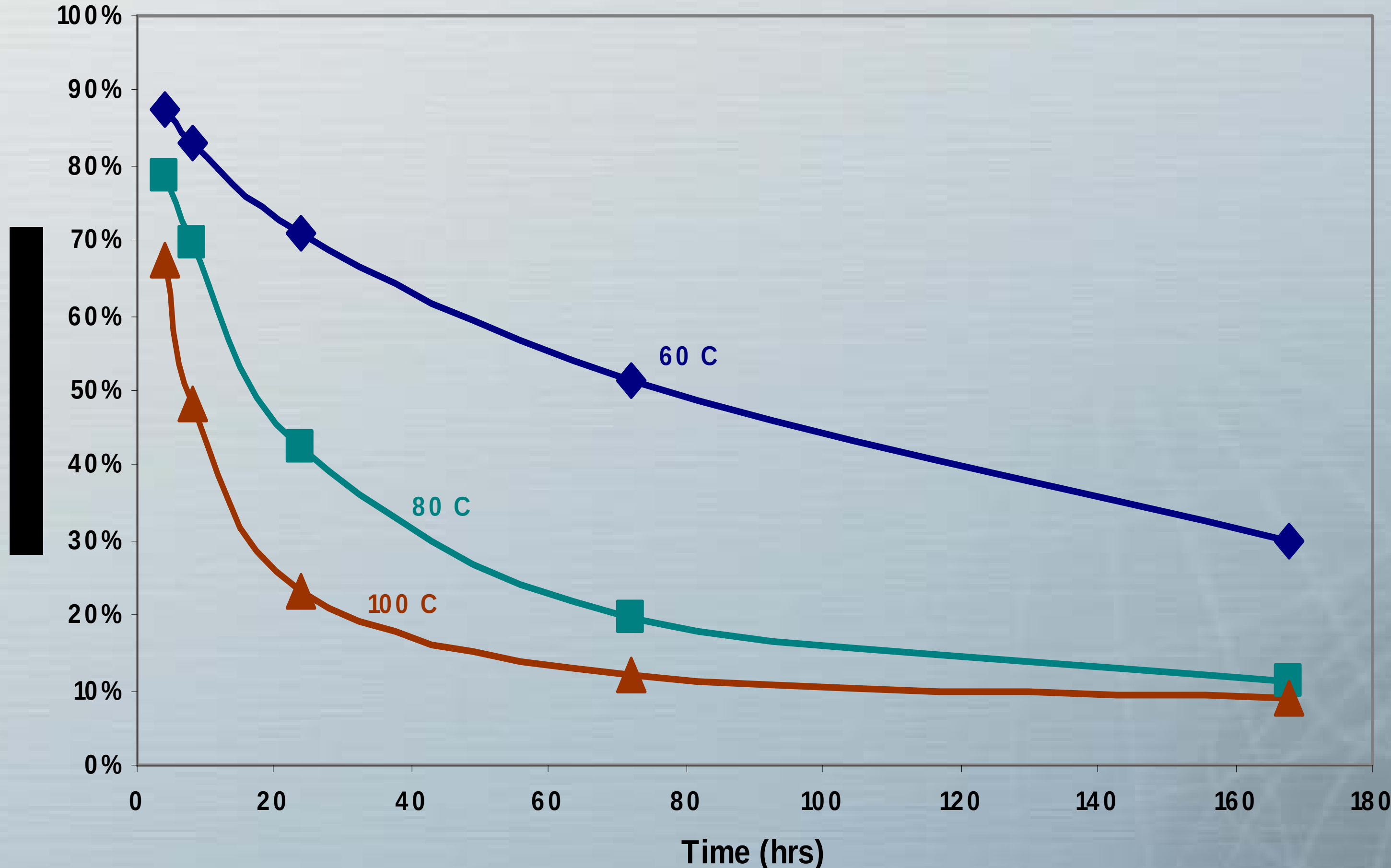
Conclusions for Al Dissolution

- Extended times (at least 72 hours) required to dissolve boehmite
- Dissolution rate is sensitive to caustic concentration and to total aluminum inventory
- Limited data available on gibbsite dissolution
- Additional boehmite testing will focus on obtaining additional characterization data to support boehmite simulant validation
- Additional gibbsite testing required to provide better basis for gibbsite dissolution performance
- Interactions between gibbsite and boehmite may be important for blended feeds.

Cr Sources

- Redox
  - Dissolves as boehmite dissolves
- S-Salt cake
  - Highly concentrated Cr stream (approximately 50% of insoluble solids are Cr).
  - Some dissolution at 100 ºC – 12% in 10 hours.
- Bi-Phosphate saltcake
  - Most samples to date blended with other sludges

Redox Chromium Solids (Mass Fraction) for 3 M NaOH in Tank S-110



Lumetta, G.J. et al., *Caustic Leaching of Hanford Tank S-110 Sludge*. PNNL-13702; Pacific Northwest National Laboratory: Richland, WA, 2001.

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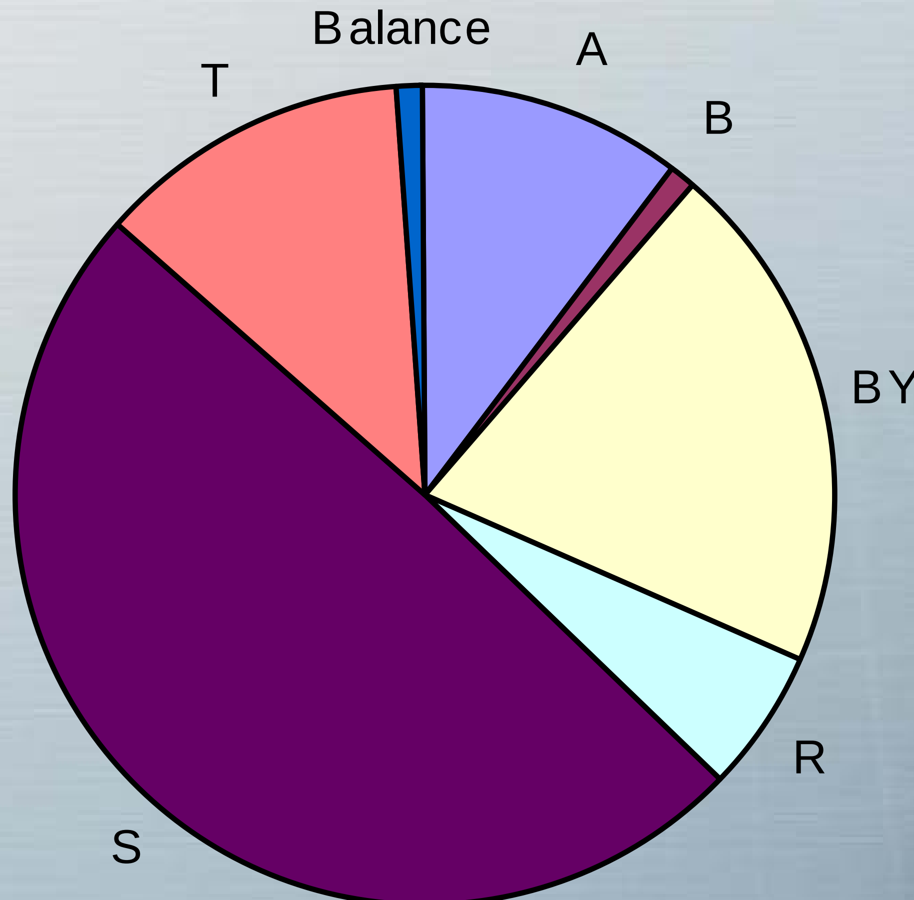
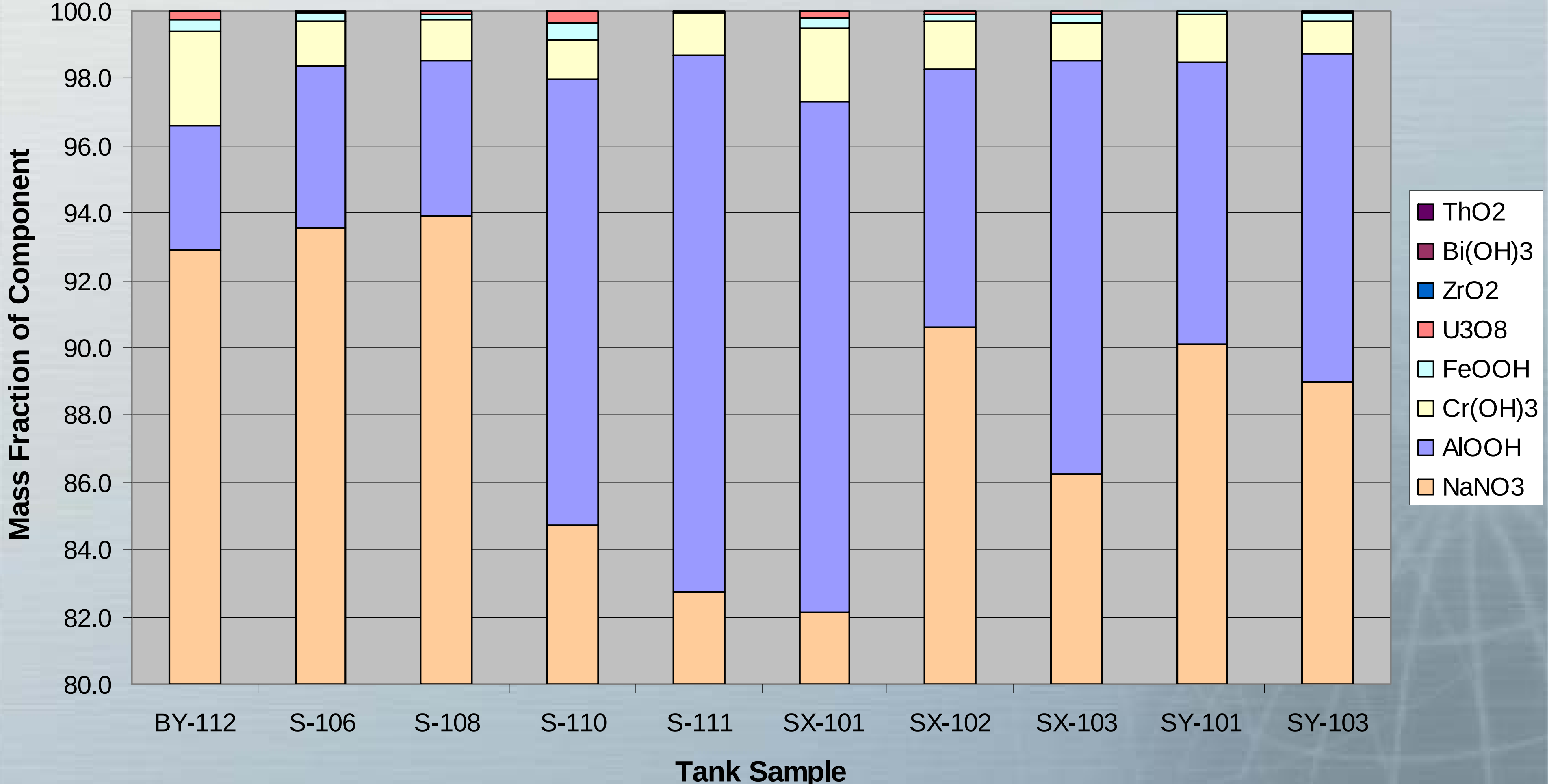
Chromium Sources in Saltcake



Composition of High Cr Saltcake (With Na)



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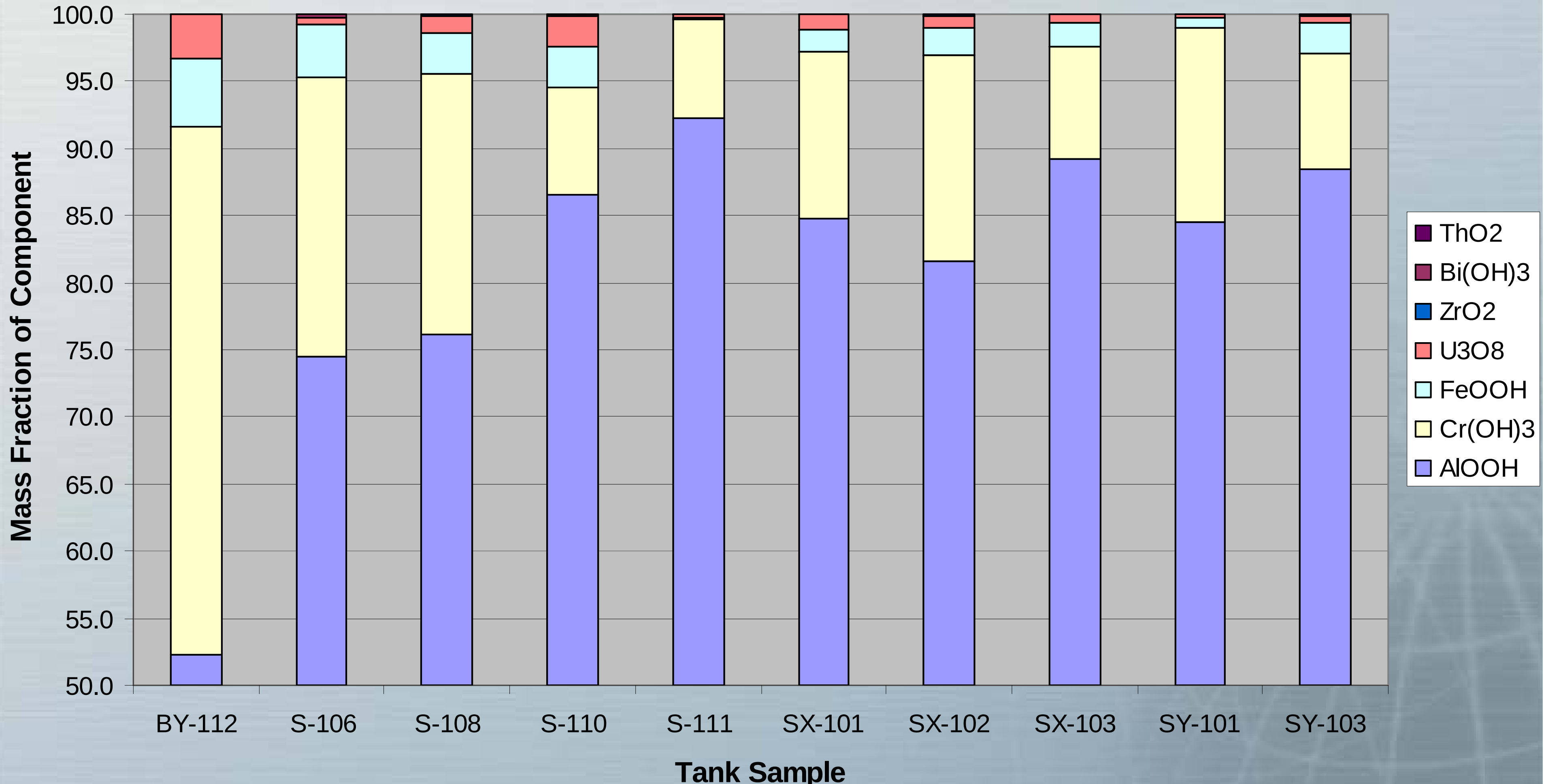
Composition of High Cr Saltcake (Without Na)



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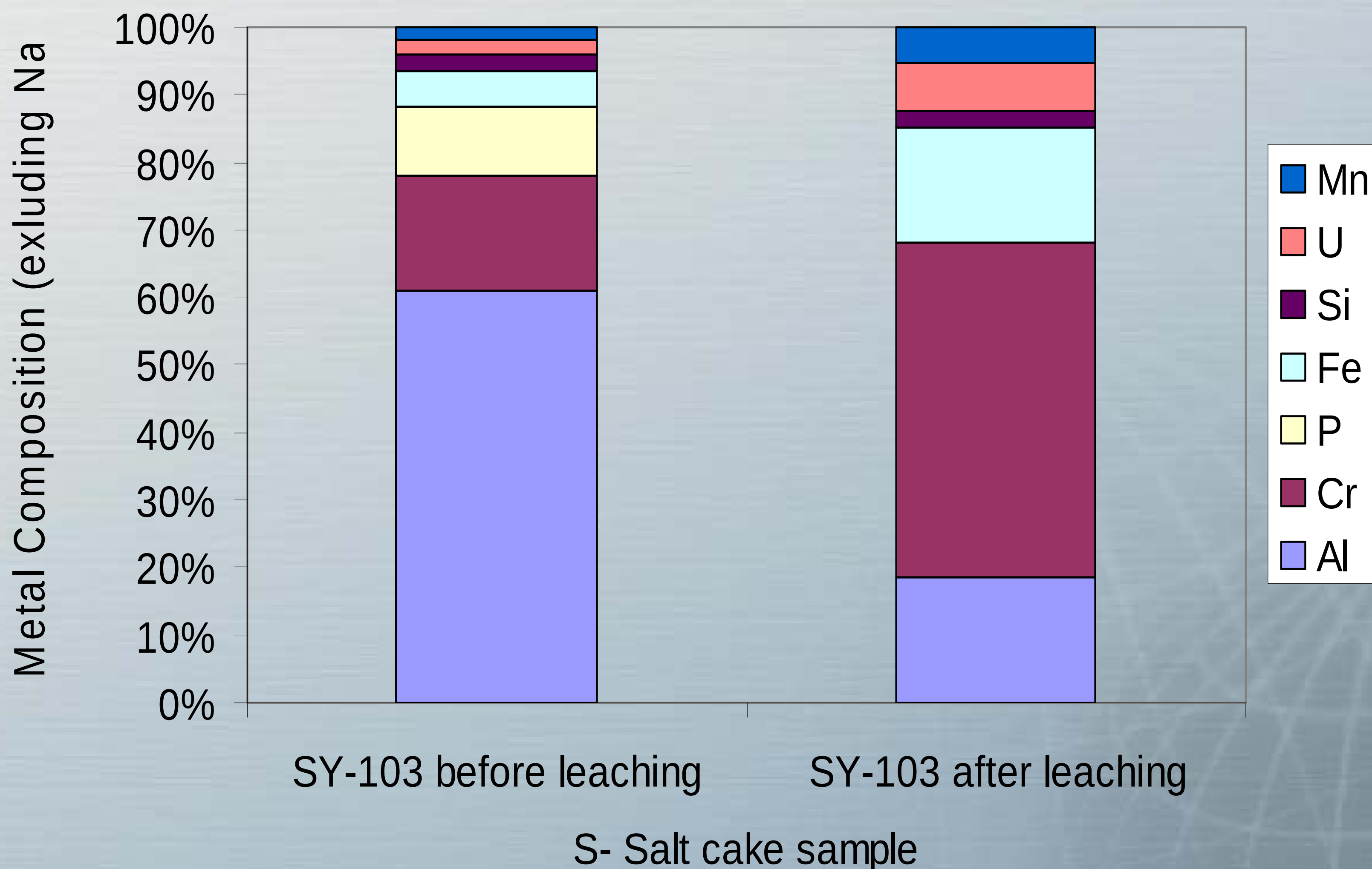
S- Saltcake composition

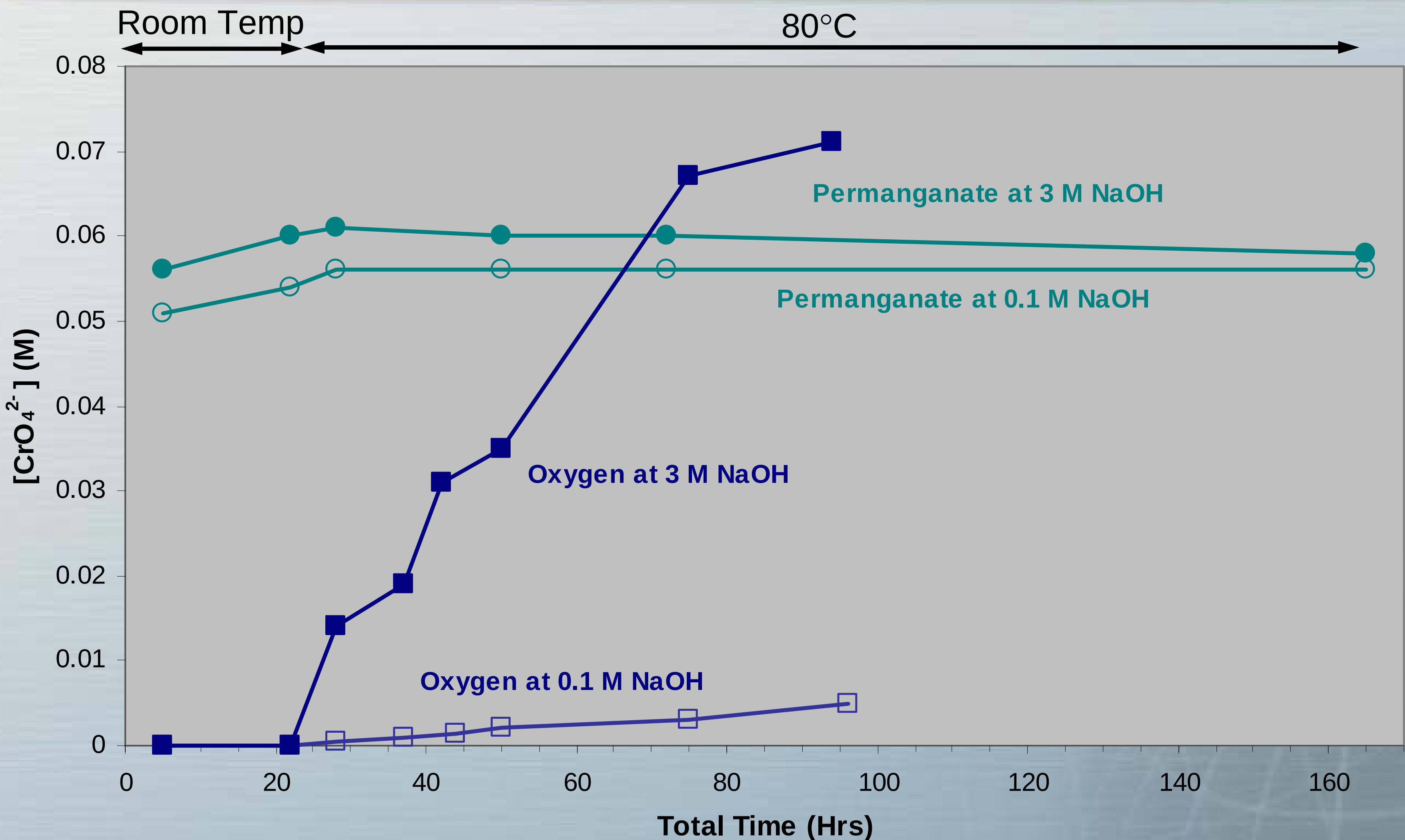
- without Na which is 75% of metal mass



Cr removal mechanism

- Cr is oxidized from Cr3+ (insoluble) to Cr6+ (soluble)
- Oxidation can be by air or by an oxidant (permanganate)
  - Permanganate oxidizes 80-95% of the available chromium
  - Rate increases with temperature
  - High hydroxide during addition results in Pu solubilization
  - No detailed rate data available
  - Air oxidation appears to be slow

Slow Apparent Oxygen Dissolution Rate, Tank U-108



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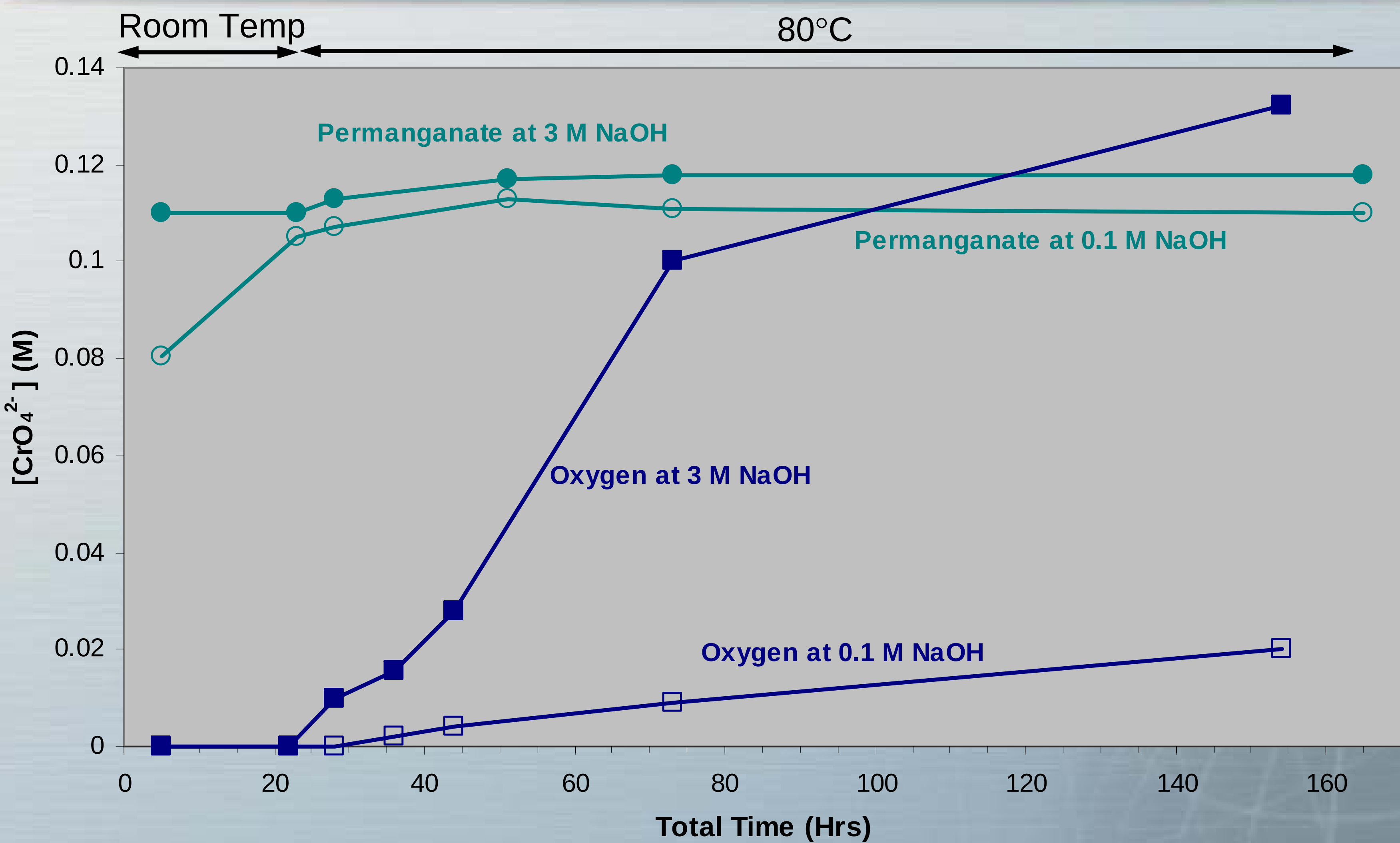
Slow Apparent Oxygen Dissolution Rate, Tank U-109



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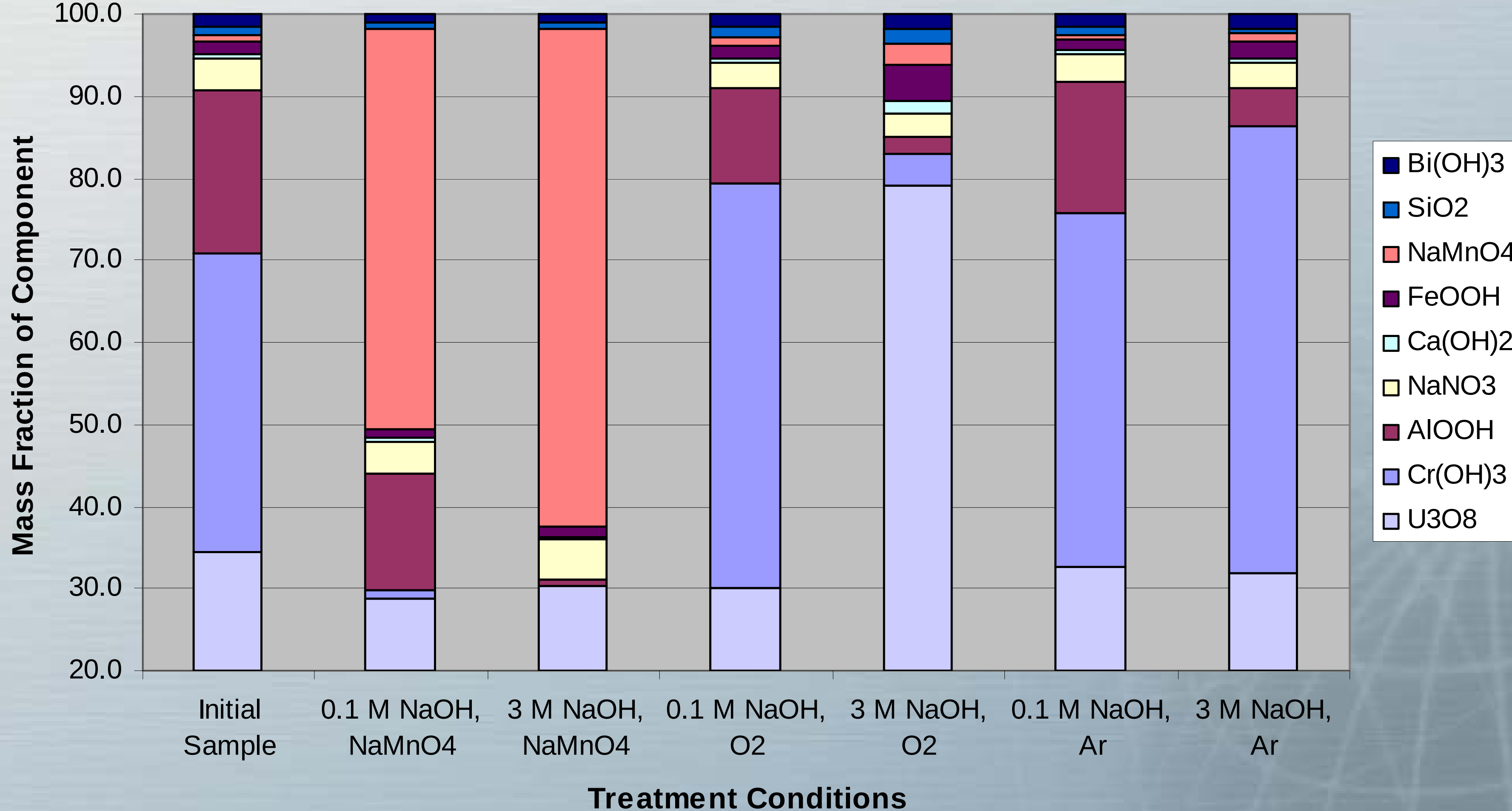
Composition of Initial and Final, Leached U-108 Samples



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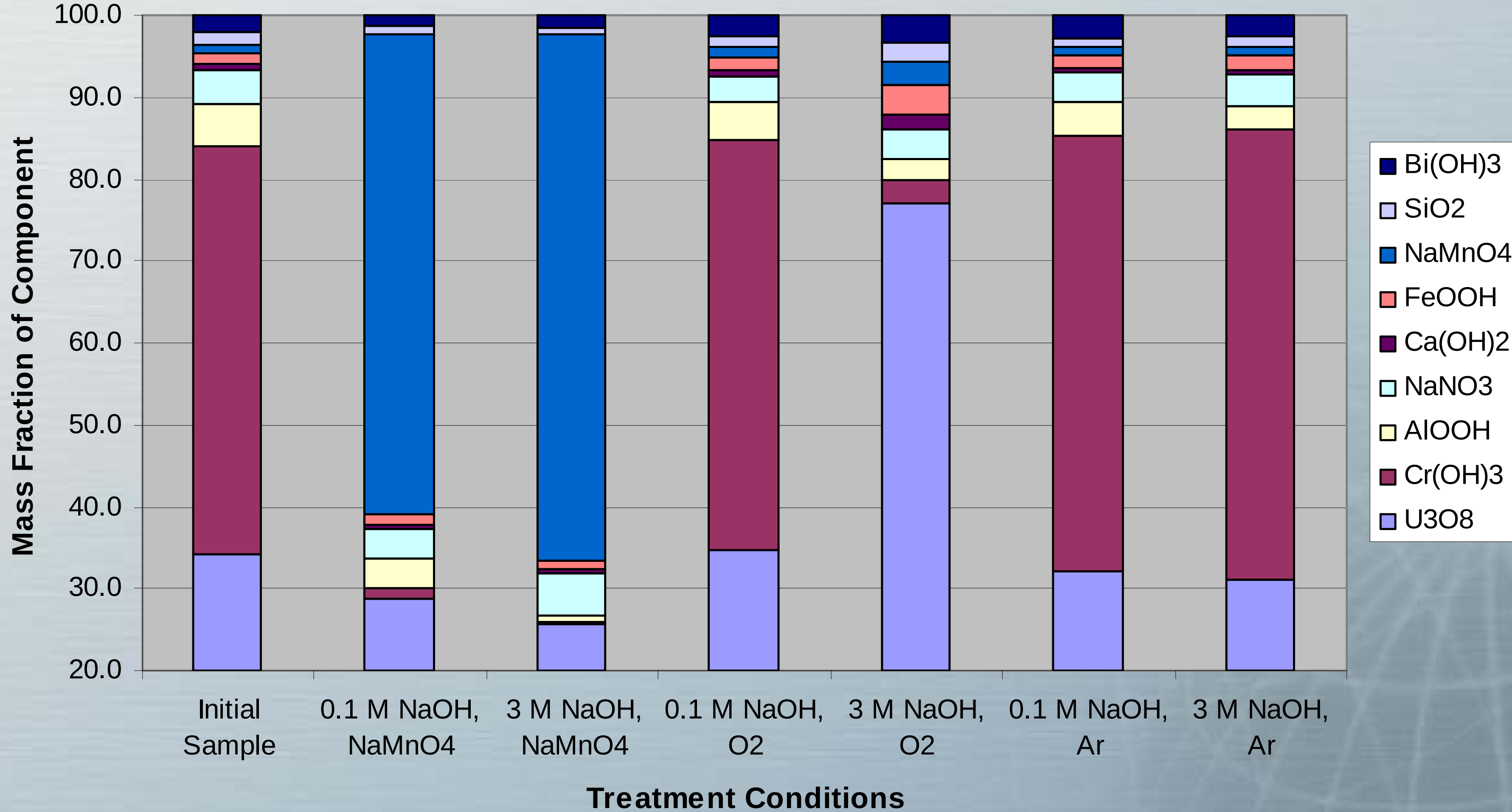
Composition of Initial and Final, Leached U-109 Samples



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Permanganate Reaction

- Cr(III) is poorly soluble in alkaline media
- Cr(III) dissolves in the presence of permanganate when the Cr(III) is oxidized to Cr(VI)
- Cr(VI) is highly soluble in alkaline media

$$Cr\left(OH\right)_3 + MnO_4^{\ -} + OH^- \rightarrow CrO_4^{\ 2-} + MnO_2 + 2H_2O$$

Conclusions for Cr Dissolution

- Air oxidation appears adequate for treatment of Cr in Hanford sludge samples
- More aggressive oxidation techniques may be required to deal with Cr present in saltcake
- Additional testing is planned to further investigate the use of permanganate to achieve oxidation of Cr in saltcake samples.
- Successful demonstration will result in dramatic reduction in the number of HLW canisters and a concomitant reduction in life cycle costs.

Testing Objectives

- Obtain leaching performance data for actual waste for the major species involved in leaching reactions
  - Supports simulant revision/development
  - Provides basis for leaching performance
- Obtain filtration performance data for a spectrum of additional actual waste samples
- Develop preliminary simulants based on available data for use in pilot scale work (pilot scale scope not covered here)
- Revise simulants based on actual waste results
- Test preliminary and revised simulants under variety of parametric conditions at the bench scale.

Overall approach

- Identify components of interest
- Identify primary sources of components of interest
- Develop component simulants for each of the components of interest
- Identify tank samples from the sources of components of interest
- Characterize and test composite samples from multiple tanks representing feed groupings.
- More details to be provided in R&D plans discussion